

1920
F.91

E. C. Fritts

Experiments on Electrosmosis

EXPERIMENTS ON ELECTROSMOSIS

BY

EDWIN COULTHARD FRITTS

B. S. Georgetown College, 1917

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN PHYSICS

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1920

1920
F91
UNIVERSITY OF ILLINOIS
THE GRADUATE SCHOOL

May 5 1920

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY EDWIN COULTHARD FRITTS
ENTITLED EXPERIMENTS ON ELECTROSMOSIS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

A. F. Carman
In Charge of Thesis

A. F. Carman
Head of Department

Recommendation concurred in*

_____	}	Committee
_____		on
_____		Final Examination*

*Required for doctor's degree but not for master's

452961



Digitized by the Internet Archive
in 2013

<http://archive.org/details/experimentsonele00frit>

T A B L E O F C O N T E N T S

I	HISTORICAL SKETCH	
	A. Electrosmosis.....	1
	B. Electrosmotic Currents.....	10
II	THEORY	
	A. Electrosmosis.....	16
	B. Electrosmotic Currents.....	18
	C. Modification of the Theory of Helmholtz for Electrosmosis Given by Lamb.....	19
III	EXPERIMENTS.....	21
IV	SUMMARY.....	29
	BIBLIOGRAPHY.....	33

PART I

Historical Sketch

A. Electrosmosis.— In the consideration of electrosmosis it is necessary to include two other phenomena which together with electrosmosis appear to be different phases of the same phenomena. The effect in any case is due to the difference of electrical potential between two substances in contact, in this case between a solid and a liquid. These later phenomena we will designate as electrosmotic currents and kataphoresis. We will at first review briefly the work which has been done in this line. In the second place we will review the theory of Helmholtz and others. Lastly, we will discuss some recent work which has been done by the author and others, and the correlation of this work with that done previously.

In this paper we will agree upon the following definitions. By electrosmosis we will understand the transfer of liquid in contact with solid walls due to a difference of potential between two points on the wall. Electrosmotic currents we will consider as the reverse of electrosmosis, or the development of electrical potential between two points on a solid wall due to the motion of a liquid along the wall. Kataphoresis we will consider as the transfer of solid suspended particles through a liquid due to a difference of potential between two points in the liquid. We will only mention kataphoresis as a kindred phenomena and confine our attention to the other two effects. It might be mentioned that Smoluchowski (1) suggests a fourth phenomena, or the production of a potential by the motion of small particles through a liquid which he calls "Kataphoretische Ströme!"

Electrosmosis was first observed by Reuss (2) in 1809 and later by Porrett (3) about 1816. Porrett noted that a transfer of water through a wall in which the pores were too small to permit the flow of water through the wall under ordinary pressures might be brought about by the application of an electrical potential. The first quantitative work was done by Wiedemann (4). Wiedemann used a piece of apparatus shown in sketch in Fig.I, Plate I. A pottery cylinder A is sealed to a glass top B which leads off through tube D to a receptacle. Inside this cylinder is placed the negative electrode N. Outside the cylinder is placed the positive electrode P and both electrodes are connected to a galvanic battery. The whole apparatus is placed in a glass jar C and both sides of the cylinder are filled with the liquid to be used. When the circuit is closed the liquid will flow over into the receptacle.

By the use of this apparatus Wiedemann showed that the quantity of liquid transferred was proportional to the time and current strength, and other conditions being constant, independent of the thickness and area of the cylinder. Table I gives data taken with this apparatus. This law was further verified by the use of another piece of apparatus shown in Fig.II, Plate I. The chambers A, B and C in a glass vessel are separated by porous walls which may be varied in area and thickness. It was found that no matter in what manner the thickness and exposed area of the walls were varied, provided the materials were the same, there appeared to be no change in the level in chamber B, showing that the same quantity of liquid was transferred through each wall.

Experiments were tried by Wiedemann with a modification of the apparatus shown in Fig.I in which the tube D was replaced by a

mercury manometer and the pressure developed studied in relation to the other conditions. The relation of this pressure to the dimensions of the diaphragm was studied by the use of the apparatus shown in Fig. III, Plate I. In this case we have two vessels A and B separated by a variable diaphragm C. Current is introduced through electrodes D. The pressures are determined by means of manometers attached to E and F. The pressure difference between the two sides of the apparatus was found to be directly proportional to the current strength and specific resistance of the liquid, inversely proportional to the exposed area and directly proportional to the thickness of the diaphragm. Considerable work was done using numerous solutions which is of little value in our present work. For some of the data taken see Tables I, II, III, IV and V.

Quincke (5) carried out further experiments of the same character by the use of capillary tubes included in apparatus shown in Fig. III Plate II. In this figure A, B and C are platinum wires sealed into a glass tube so as to make possible the use of different lengths of the tube. A scale was attached to the tube at L so that the movement of the meniscus of the liquid could be measured. The flask D attached was large enough that a marked change in the position of the meniscus would produce no appreciable change in the level of the liquid in the flask. In use the tube was tilted by a small angle θ so that a compensating pressure difference might be developed. The tube was cleaned thoroughly before using and it was found that by using a glass which was a good dielectric and a battery of Leyden jars as the source of current the pressure developed was directly proportional to the quantity of electricity discharged, as measured by a Lane's Unit Leyden jar, and independent of the

time of discharge. The pressure was further, directly proportional to the length of the tube carrying the current. When a battery of 40 to 50 Grove cells was used it was found that the pressure was directly proportional to the current strength and for different lengths of the tube directly proportional to the e.m.f. In general the transfer took place from the positive to the negative electrode. The effect was roughly inversely proportional to the square of the radius of the tube and decreased as the conductivity of the liquid increased. Experiments were performed using different liquids such as methyl and ethyl alcohol and others in which the transfer was, in general, from positive to negative. A certain sample of impure alcohol and a solution of turpentine in alcohol used in a tube lined with shellac gave the transfer in the reverse direction.

We see from the above that one might represent the results stated above, for the case of the transfer of a liquid through a diaphragm by the equation

$$M = KI$$

where K is a constant of proportionality. The pressure developed might also be represented by

$$P = \frac{CITS}{A} ,$$

or

$$P = CE.$$

In these equations P represents the pressure, I the current, E the e.m.f., S the specific resistance of the liquid, A the area, and T the thickness of the diaphragm.

Quinke performed numerous experiments with a modification of his apparatus described above, the results of which are given in Table VI. Fig.IV, Plate I, shows a simpler piece of apparatus

used by Quincke.

Perrin (6) has also performed extensive experiments on electrosmosis using apparatus the essential parts of which are shown in Fig. IV, Plate II. A diaphragm of powdered material, shown at C, is placed in one arm of a U-shaped tube, electrodes are sealed in on either side of ~~this~~ diaphragm and the open arm of the tube is led off to a capillary tube graduated in cubic centimeters. The figure shows the capillary tube tilted at a small angle θ to the horizontal. In the use of this apparatus, to study the volume transfer of liquids this tube was placed horizontal. Quite different materials were used in the construction of the diaphragms such as Al_2O_3 , naphthaline, CrCl_3 , AgCl and BaSO_4 . The diaphragms were from 10 to 12 cm. thick. By the use of weak solutions of acids and alkali Perrin was led to the conclusion that the potential difference of the double layer was dependent upon the nature of the solution alone. His work, which is in marked contradiction to the work of numerous others, would lead to the idea that the potential difference is due to the relative diffusion velocities and sizes of the ions present in the solution.

Starting with a weak solution of KOH , Perrin noted a transfer in the direction of the positive current. As the solution was made more concentrated the effect was diminished and became nearly equal to zero when neutral. Upon making the solution acid the transfer was reversed in direction, becoming larger as the concentration was increased. With a neutral solution the transfer was practically zero and for weak acid solutions the transfer was in the reverse direction. Perrin explained this by assuming H and OH ions, small

in size as compared with the other ions present. In such a case they would get nearer to the wall and would impart to the layer of liquid nearest the wall a charge of the same sign as that which they carried. A brief table of the results obtained by Perrin is given in Table VII.

Some work has been done by Freund (7), Kühne (8), and deBois Reymond (9), but adds nothing of value to this discussion and will be omitted.

Tables I, II, III, IV, and V, refer to the work of Wiedemann, Part I, Section A.

The liquid used in all these experiments was pure water.

TABLE I

Units: i current not given; m in grams transferred per unit time.

i	144.00	108.00	83.00	60.00	48.00	36.00	29.00
m	17.77	13.26	10.59	7.46	5.89	4.47	3.38
10m/i	1.23	1.23	1.27	1.24	1.23	1.24	1.17

TABLE II

Units: i current not given; p pressure not given.

i	128.00	109.00	97.0	73.00	65.30	58.30	45.00	26.50	13.00
p	176.50	147.50	132.5	100.50	89.00	80.50	61.00	37.50	19.50
p/i	1.38	1.35	1.37	1.38	1.36	1.38	1.36	1.41	1.36

TABLE III

Units: S spec. resist.; i current not given; p pressure not given.

% Solution	16.25	9.22	6.60	3.40	1.80
S	18.00	27.00	32.50	55.50	100.00
p/i	1.35	1.98	2.44	3.79	6.80
p/iS	7.50	7.33	7.50	6.83	6.80

TABLE IV

Units: A area in sq.cm.; i current not given; p pressure not given.

A	1.00	0.70	0.40	0.20
p/i	1.37	1.80	3.42	6.00
Ap/i	1.37	1.26	1.37	1.20

TABLE V

Units: T thickness in mm.; i current not given; p pressure not given.

T	8.00	4.00	1.70 to 2.00
p/i	3.30	1.62	0.73
p/iT	0.41	0.40	0.43 to 0.36

Table VI refers to the work of Quincke, Part I, Section A.

TABLE VI

Units: L, length of tube in mm.; r, radius of tube in mm.; θ , the angle of elevation of tube L with horizontal; n, the number of Grove cells used; h, the deflection of the meniscus.

$$b = 0.0437 \frac{r^2 h \sin \theta}{n}$$

L	2r	θ	n	h	b x 10 ⁴
96	0.376	9° 06.5'	81	20.15	0.607
96	0.376	8° 52.8'	78	19.51	0.595
96	0.376	8° 49.7'	78	18.07	0.555
100	0.897	4° 26.5'	78	7.33	0.640
100	0.897	5° 14.0'	78	5.85	0.601
100	0.897	5° 26.5'	80	5.87	0.597
305	1.775	8° 49.7'	78	0.94	0.644
230	1.885	2° 38.5'	78	2.38	0.549
230	1.990	2° 38.5'	78	2.31	0.590

Mean Value of b	Tube	Liquid
0.0000597	Glass	Water
0.0000792	Shellac coated glass	Water
0.0000545 to 0.0000384	Silvered glass	Water
0.0000341	Glass	Absolute Alcohol

Table VII refers to the work of Perrin, Part I, Section A.

TABLE VII

Diaphragm	Solution	Concentration in G. Mol. per L.	Transfer per min.
Al_2O_3	HNO_3	0.002	-110
	HCl	0.0004	- 70
	NaOH	0.002	+ 55
	NaOH	0.004	+ 90
C_{10}H_8	HCl	0.01	- 39
	HCl	0.02	- 38
	HCl	0.001	- 28
	HCl	0.0002	- 3
	KOH	0.0002	+ 29
	KOH	0.001	+ 60
	KOH	0.02	+ 60
CrCl_3	HCl or HBr	0.001	- 95
	KOH or LiOH	0.002	+ 85
BaSO_4	HCl	0.002	- 9
	KOH	0.004	+ 7
AgCl	HCl	0.002	- 30
	KOH	0.002	+ 85
Sulphur	HCl	0.02	- 22
	HCl	0.002	0
	KOH	0.002	+ 65
	KOH	0.02	+ 92
Carborundum	HCl	0.02	- 10
	HCl	0.008	0
	HCl	0.002	+ 15
	Water	0.0000	+ 50
	KOH	0.0002	+ 60
	KOH	0.002	+105
Gelatine	HCl	0.02	- 22
	KOH	0.01	+ 35
Cellulose	HCl	0.033	0
	HCl	0.002	+ 20
	KOH	0.002	+ 70

B. Electrosmotic Currents.- About 1860 Quincke (10) conducted a series of experiments on electrosmotic currents, using the apparatus shown in Fig. I, Plate II. The essential features of the apparatus are that a porous diaphragm C is sealed tightly between the ends of two glass tubes A and B, through which water is caused to pass by hydrostatic pressure. The resultant current is measured by means of a galvanometer E connected to platinum electrodes D and F sealed into the glass tubes. Another arrangement of apparatus was used which was very similar to that used by Wiedemann shown in Fig. I, Plate I. In this apparatus the tube D was replaced by a closed tube in which pressure was developed by the electrolysis of water. This pressure was measured by a mercury manometer and caused the water to pass through the wall. The resultant e.m.f. was measured by the Poggendorff compensation or potentiometer method. Quincke found that the addition of an acid or a salt produced a marked decrease in the result. The addition of a weak solution of alcohol produced a slight increase. The e.m.f. was shown to be independent of the dimensions of the diaphragm, and directly proportional to the pressure forcing the water through the wall. Certain data taken by Quincke with this type of apparatus is given in Table VIII.

Zöllner (11) carried out similar experiments, using capillary tubes in the place of the diaphragms. In the case of tubes which obeyed the law of Poiseuille, Zöllner found that the e.m.f. was directly proportional to the pressure and independent of the dimensions of the tube. These tubes were from 10 cm. to 55 cm. in length, and from .152 mm. to .949 mm. in diameter. Pressures up to 480 mm. of mercury were used. The e.m.f. was measured with a

quadrant electrometer.

Dorn (12), using tubes of lengths from 300 to 500 mm. and of cross-section from .0538 sq.mm. to .2301 sq.mm., obtained by the use of pressures up to two and a half atmospheres, values of the e.m.f. up to 3.55 Daniells.

More recent work has been done by Cameron and Oettinger (13) in which they attempt to settle a contradiction arising between the theories of Helmholtz and Perrin, which contradiction will be discussed later. The work was done with an arrangement of apparatus very similar to that of Quincke, using capillary tubes and forcing water through by means of compressed air. Quite extensive work was done using dilute solutions. Experiments were performed in which it was shown that if there were any variation of the effect due to temperature it was of such a magnitude as to be hidden by other variations. It was shown that the e.m.f. decreased when the water was allowed to flow for a period of time. The original value of the e.m.f. was again obtained after the tube had been cleaned. A synopsis of the results obtained in this work is given in Table IX.

We will find in the development of the theory for electrosmosis and electrosmotic currents* in a capillary tube that there should exist a relation given by

$$\frac{M}{I} = \frac{E}{P} ,$$

where M is the quantity of liquid transferred by the current I in a unit time, and E is the electrosmotic e.m.f. developed by a pressure P. Using the same apparatus in both experiments, Saxen (14) has attempted to verify this equation, and the results are given in Table X. From this table it may be seen that there is an equality

between the two quantities within an error commensurate with the experimental error, so that the phenomena are completely reversible.

TABLE VIII

Table VIII refers to the work of Quincke, Part I, Section B.

Material of Diaphragm	e.m.f. in Daniells per atmosphere
Sulphur	977.07
Quartz Sand	620.49
Shellac Powder	330.01
Silk	115.45
Burned Clay	36.15
Asbestos	22.15
Porcelain	19.86
Ivory	3.10
Animal Tissue	1.51

Note: The liquid used in each case was water.

TABLE IX

Table IX refers to the work of Cameron and Oettinger, Part I, Section B.

Using pure water in a glass tube.

Pressure in mm. of Hg.	e.m.f. in Volts	e.m.f./Pressure $\times 10^3$
87.6	0.593	6.76
233.4	1.307	5.60
146.7	0.971	6.62
350.0	2.100	6.00
96.1	0.490	5.10

Using glass tube and KCl solution N/3000

$$\text{e.m.f./Pressure} \times 10^3 = 1.15 \text{ to } 1.7$$

Using Solutions to Determine $(\phi_1 - \phi_a)$

Solution	Concentration	$(\phi_1 - \phi_a)$ in Volts
HCl	N/5000	3.52 to 4.60
Acetic Acid	N/2000	3.95 to 4.20
HCl	N/2500	2.80 to 4.22
NH ₄ OH	N/5000	4.72 to 5.45
KOH	N/2000	6.44 to 7.23
KCl	N/2000	4.73 to 4.84

TABLE X

Table X refers to the work of Saxen, Part I, Section B.

Solution	P	$E \times 10^6$	I	M	Time	M/I	E/P
ZnSO ₄	34.7	4.93	228.4	1.531	1208	0.3768	0.3698
ZnSO ₄	39.6	5.18	232.0	1.653	1259	0.3866	0.3862
CuSO ₄	-	-	-	-	-	0.3850	0.3852
CdSO ₄	-	-	-	-	-	0.5823	0.5800

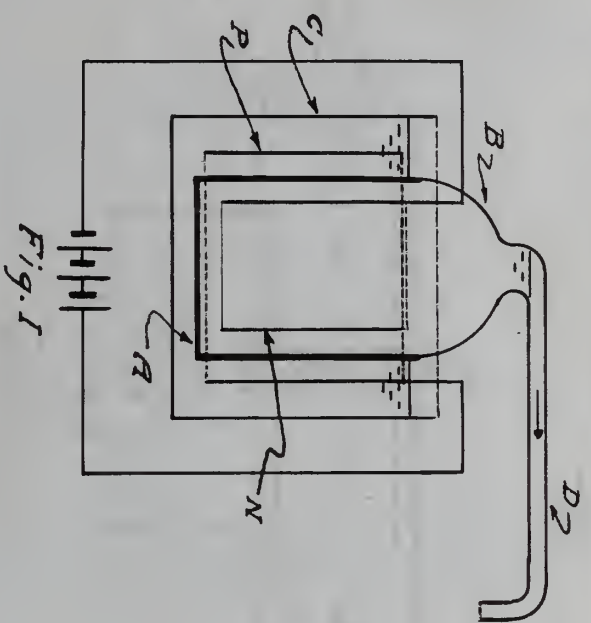


Fig. I

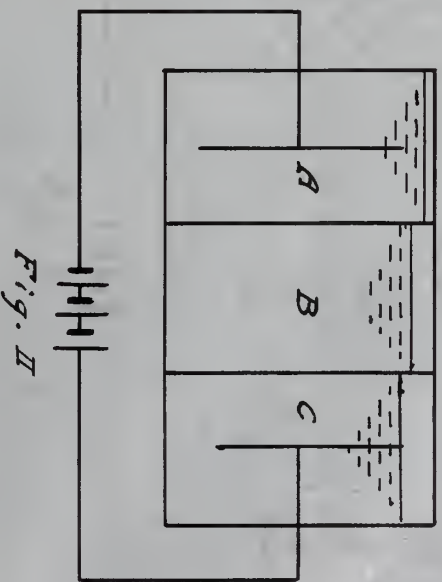


Fig. II

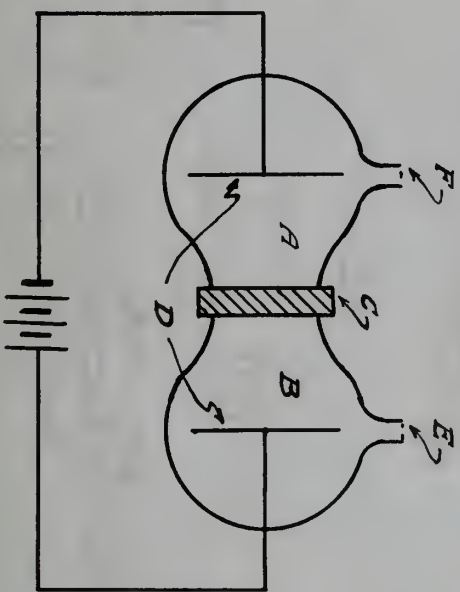


Fig. III

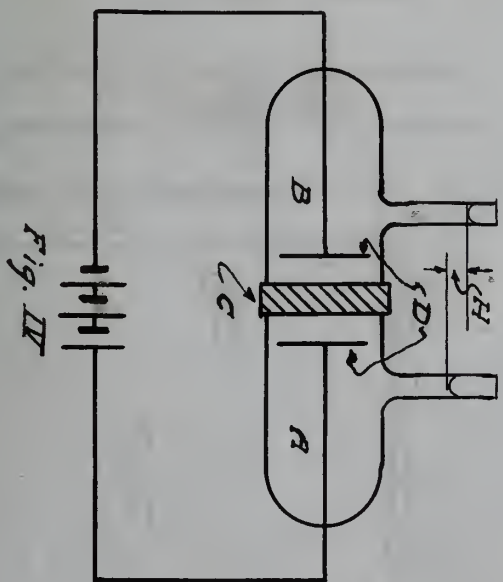
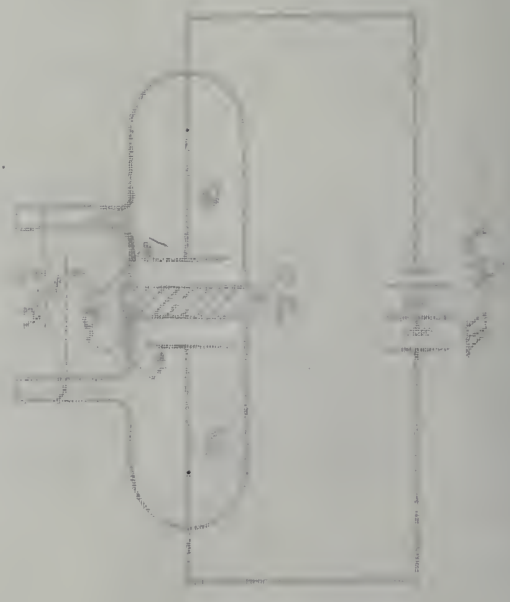
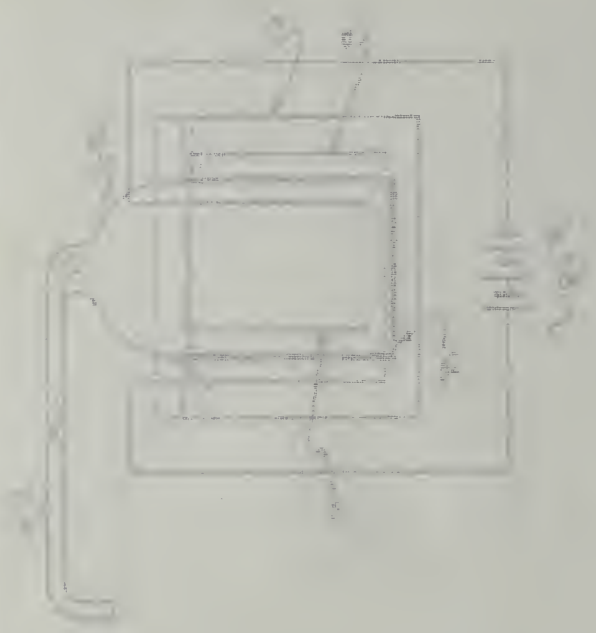
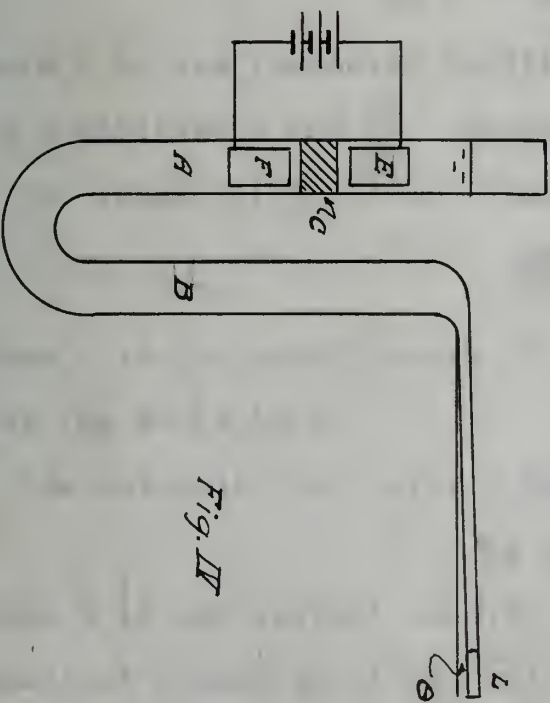
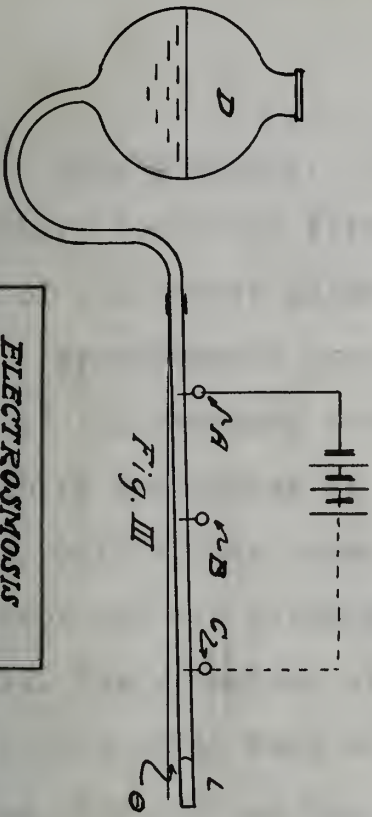
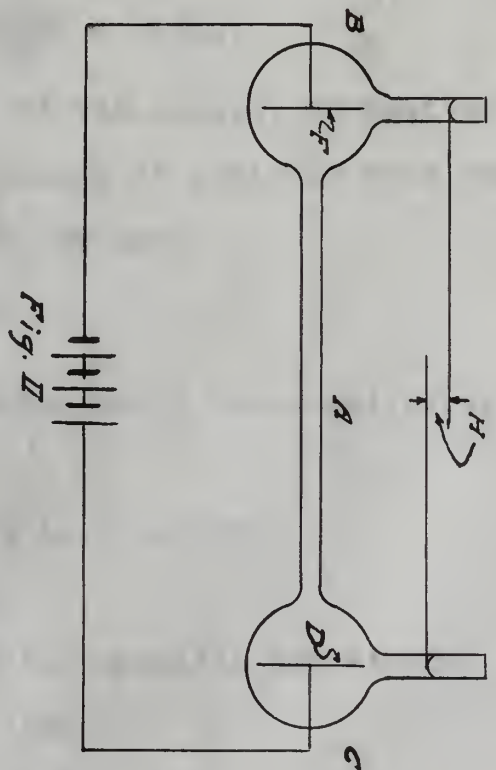
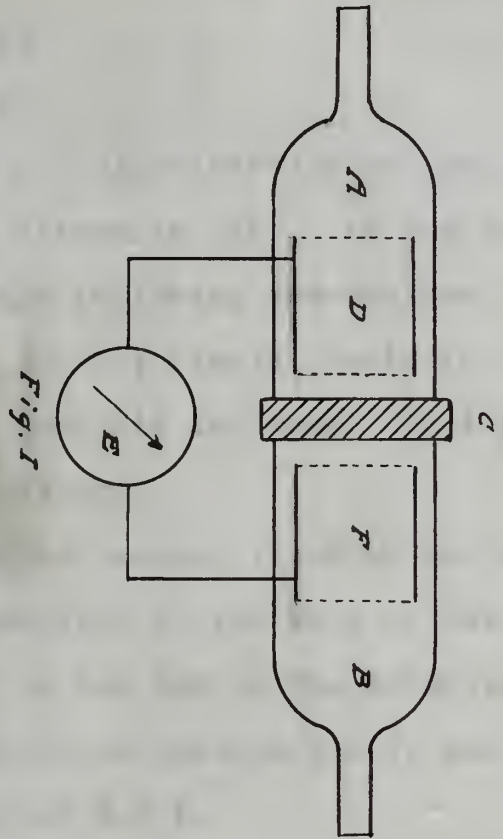
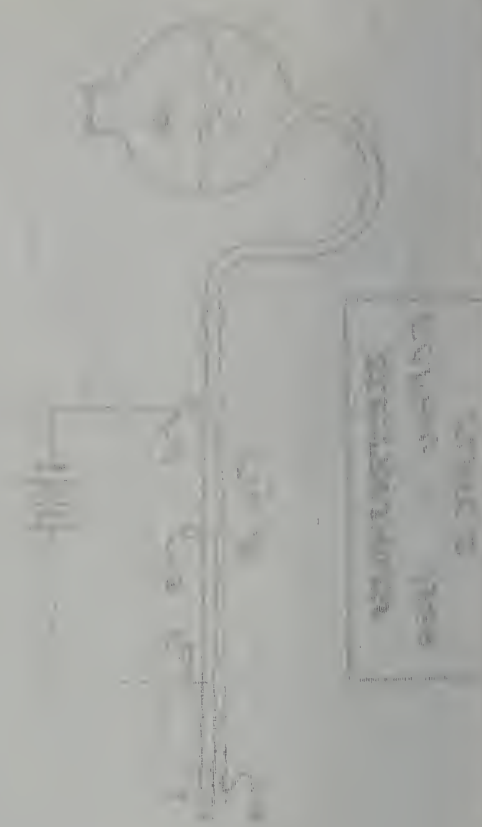


Fig. IV

1880
 1881
 1882
 1883
 1884
 1885
 1886
 1887
 1888
 1889
 1890
 1891
 1892
 1893
 1894
 1895
 1896
 1897
 1898
 1899
 1900







1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100.



PART II

Theory

A. Electrosmosis.— The theory for electrosmosis as applied to capillary tubes was first given by Helmholtz (15). In the development of his theory Helmholtz made the following assumptions.

I. Hydrodynamic equations hold for the liquid, including the region of the boundary between the liquid and the tube. This region Helmholtz designates as the double-layer.

II. Only a thin layer of the liquid remains fixed to the wall of the tube and all streamlines are parallel to the axis of the tube.

III. The potential at any point is the sum of the potential in the liquid if it were at rest, without an applied e.m.f. and the change in potential due to the applied e.m.f.

In order to apply the hydrodynamic equation which for our problem takes the form

$$X - \frac{dP}{dx} = -\lambda \left(\frac{d^2u}{dy^2} + \frac{d^2u}{dz^2} \right) = -\lambda \Delta u, \quad (1)$$

where λ is the viscosity coefficient of the liquid, we must evaluate the quantities X and $\frac{dP}{dx}$. Since the change of pressure with respect to the length of the tube is constant, we have

$$\frac{dP}{dx} = \frac{P}{L} \quad (2)$$

where L is the total length of the tube, and P the total pressure over the whole tube.

The potential fall over a length x is given by

$$\phi_r = -isx \quad (3)$$

where i is the current density and s the specific resistance. The resultant potential at any point is then

$$U = \phi_i + \phi_r = \phi_i - isx \quad (4)$$

where ϕ_i is the potential in the interior of the tube when no external e.m.f. is applied and is assumed to be constant except in the region of the double-layer where there is a rapid change.

The force on the charge per unit volume e is given by

$$X = eis$$

$$\text{or, since} \quad K \Delta U = -4\pi e \quad (5)$$

$$X = \frac{-isK \Delta U}{4\pi} \quad (6)$$

and the hydrodynamic equation becomes on substitution

$$\frac{isK}{4\pi} \Delta U + \frac{P}{L} = \lambda \Delta U. \quad (7)$$

We may consider u , the velocity, to be composed of two components, u_p due to the hydrostatic pressure, and u_ϕ due to the e.m.f. applied. We may then divide the equation into two equations, each representing the equation of one of these components, as follows:

$$\frac{isK}{4\pi} \Delta U = \lambda \Delta u_\phi \quad (8)$$

$$\text{and} \quad \frac{P}{L} = \lambda \Delta u_p. \quad (9)$$

A solution of (8) is then given by

$$u_\phi = \frac{isK}{4\pi\lambda} U + F(x) + C. \quad (10)$$

Since we must consider the velocity independent of x

$$F(x) = 0, \quad (11)$$

and taking the boundary conditions at the wall where $u_\phi = 0$ and

$$U = \phi_a$$

$$0 = \frac{isK}{4\pi\lambda} \phi_a + C,$$

or

$$C = -\frac{isK}{4\pi\lambda} \phi_a. \quad (12)$$

Substituting these values together with u_p as the solution of (9), we have for the resultant velocity

$$u = u_p + \frac{isK}{4\pi\lambda} (\phi_i - \phi_a).$$

If we assume that there is a slight slip we must add the term

$$u_s = C \frac{du}{dN}$$

where C will be the slipping coefficient. Equation (12) then becomes

$$u = u_p + \frac{isK}{4\pi\lambda} (\phi_i - \phi_a) + C \frac{du}{dN}. \quad (13)$$

We will now apply the general equation to the particular cases of electrosmosis. Assuming $C = u_p = 0$, we have the quantity of liquid carried over per unit time by the applied e.m.f., considering the density as unity,

$$M_\phi = \frac{Is}{\lambda} \frac{K(\phi_i - \phi_a)}{4\pi} = \frac{ER^2}{4\lambda L} \frac{K(\phi_i - \phi_a)}{4\pi} \quad (14)$$

where I is the current strength, E the e.m.f. applied, and R the radius of the tube. If the transfer of liquid should take place until the effect of the e.m.f. is balanced by the pressure developed, and acting in the opposite direction, we have

$$M_\phi = M_p.$$

By the law of Poiseulle

$$M_p = \frac{P R^4 \pi}{8\lambda L} = \frac{ER^2 K(\phi_i - \phi_a)}{4\lambda L}, \quad (15)$$

or

$$P = \frac{2EK(\phi_i - \phi_a)}{\pi R^2} \quad (16)$$

B. Electrosmotic Currents.— The volume of liquid carried through a tube per unit time is given by

$$V = \iint \frac{du}{dN} N dN ds \quad (17)$$

where u is the velocity, N the normal direction from the wall of the tube directed inward, and ds an element of arc. The charge of electricity carried over per unit time is further given by

$$I = \iint e \frac{du}{dN} NdNdS \quad (18)$$

where e is the unit volume charge. We may substitute the value of e as given by Poissons equation,

$$e = - \frac{K}{4\pi} \frac{d^2\phi}{dN^2},$$

and obtain the equation for current

$$I = \int \frac{du}{dN} dS \int eNdN = \frac{1}{\lambda} \int \lambda \frac{du}{dN} dS \left(- \frac{K}{4\pi} \int \frac{d^2\phi}{dN^2} NdN \right), \quad (19)$$

where λ is the viscosity coefficient. If we perform the last integration by parts, setting $U = N$, and $dV = dN$, we obtain

$$I = \frac{1}{\lambda} \int \lambda \frac{du}{dN} dS \left(- \frac{K}{4\pi} \left(N \frac{d\phi}{dN} \right)_0^i + \frac{K}{4\pi} (\phi_i - \phi_a) \right),$$

where i is the value of N at the point where the potential becomes constant. In the case of this limit $\frac{d\phi}{dN} = 0$. From the definition of λ we will see that $\lambda \int \frac{du}{dN} dS$ is the frictional force acting on a unit length of the liquid and is equal to PA/L . Our current is then given by

$$I = \frac{PAK(\phi_i - \phi_a)}{4\pi\lambda L},$$

or

$$E = \frac{ILs}{A} = \frac{KPs(\phi_i - \phi_a)}{4\pi\lambda}. \quad (20)$$

C. Modification of the Theory of Helmholtz for Electrosmosis given by Lamb.— Lamb (16) considered the double-layer as a condenser whose plates were separated by a distance d , the thickness of the double-layer. The capacity of such a condenser per unit area is

$$C = \frac{K}{4\pi d}$$

and the charge

$$Q = \frac{K(\phi_i - \phi_a)}{4\pi d}.$$

If then we have a potential gradient $\frac{d\phi}{dx}$, the tangential force on

the inner plate is

$$X = \frac{K(\phi_i - \phi_a)}{4\pi d} \frac{d\phi}{dx} = Bu,$$

where B is a coefficient to be discussed later. The velocity of the inner plate is then

$$u = \frac{K(\phi_i - \phi_a)}{B4\pi d} \frac{d\phi}{dx} = \frac{K(\phi_i - \phi_a)}{B4\pi d} \frac{Is}{A}.$$

If the density is unity, the volume of liquid transferred per unit time is

$$V = M = \frac{IsK(\phi_i - \phi_a)}{B4\pi d}. \quad (21)$$

If we set $B = \lambda/l$, we then see that the equation agrees with that of Helmholtz except for the factor l/d . The remaining equations of Helmholtz may also be developed in the same manner and the same difference in the factor l/d found.

The difference between the theories of Helmholtz and Lamb lies in the assumption of Helmholtz that the hydrodynamic equations have no discontinuity in the region of the double-layer. This assumption is opposed by Lamb on the basis of the fact that the thickness of the double-layer is of the order of magnitude of the molecule in which case we cannot assume that our general laws of hydrodynamics hold. We see that if $l = d$, the two theories lead to the same result. Since the equations of Lamb contain two indeterminate quantities $\phi_i - \phi_a$ and l/d we cannot determine the value of either without further relations. If the value of l/d is near unity it is also difficult to detect experimentally a difference between the two theories.

PART III

Experiments

The work which has been done at the University of Illinois arose from the possibility of applying the electrosmotic current effect to the detection of sound waves in water. The first work was done by the late C.E. Pike under the direction of Professor Carman in the summer of 1918, and serves as valuable preliminary work to that discussed here. The results of Mr. Pike's work are, as far as they go, in accord with the results obtained later.

Upon investigation of the literature the contradiction between the work of Perrin, Helmholtz and others was discovered, which difference was based primarily upon the influence of the wall. To determine, if possible, any influence which the wall might have in the phenomena, an extended series of experiments were performed, using first the electrosmotic current effect as applied to capillary tubes of various materials. These tubes were of the same order of length and diameter and were used under the same conditions as far as possible. Various methods were used to force the water through the tubes. The most satisfactory method is shown in sketch in Fig.I, Plate III. Considering this figure, we have at C the capillary tube which is connected to the enlarged tube G, which in turn is connected to the mercury manometer M and the closed flask B. The flask B is connected to the syphon S by means of which the pressure in G is decreased.

This method was very effective and easy to manipulate. Very constant pressures were also obtained, which was more difficult with other forms of apparatus. The pressure **M** was noted and corrected for the difference of level between G and A. The e.m.f. between

the platinum electrodes D and F was measured by means of a Wolff potentiometer in some cases, and by a quadrant electrometer in other cases.

Tubes were prepared from sulphur, rosin and Bank of England sealing wax, by casting rods of the materials in glass tubes as in the case of sulphur and Bank of England wax, or in oiled paper as in the case of rosin. After a rod had been cast it was removed from the mold and laid in a horizontal position. A German silver wire (No. 22 B. & S.) was passed over a pulley and stretched in a position such that when heated by an electric current it would melt its way into the rod and reach a position along its axis. The current was then removed and the rod allowed to cool. Again the wire was heated and just as it was loose from the wall it was cut behind the rod so that the hanging weight would draw it quickly from the rod. In this manner quite uniform tubes were produced about 1 mm. in ^{internal} diameter. It was quite difficult to produce tubes of very great length although a few were obtained. The tubes so formed were sealed into glass tubes to give them mechanical strength and included in the apparatus.

It was found that if the tubes satisfied the conditions for the law of Poiseuille the e.m.f. developed was directly proportional to the pressure applied to the ends of the tube. This pressure was obtained with a degree of approximation in that no correction was made for the kinetic energy imparted to the liquid, which represents a certain decrease in pressure. If we consider the curves in Plate IV which represent the data taken in these experiments and which is given in Table XI, we see that for the most part they intersect the e.m.f. axis not at the origin but at some positive

value. This result can not be due to the error mentioned above in the measurement of the pressure, and this would produce a negative intercept on the e.m.f. axis. This result was obtained in nearly all cases and must be due to some form of polarization. It was noted in most cases that if the pressure was increased from zero to some maximum value and then decreased the slope of the curve in the latter case was less and the curve intersected the e.m.f. axis at a higher value than zero from which it started. Attempts were made to determine accurately the points near the origin but this was found difficult. Curve 4 gives the characteristic curve for a tube which is not of sufficient length to obey the law of Poiseulli. No data for ordinary glass is given as values of the e.m.f. obtained in their use were quite small as compared with those obtained with pyrex and Jena glass. In general it was found that water gave the highest values of the liquids used. All other liquids gave very small results, an example of which is given in Curve 8 in which alcohol was used in a Pyrex glass tube. The values of the e.m.f. were quite difficult to repeat and the data given which in any case is that of one experiment might be considered only approximate. It seems that the conductivity of the liquid, water in most cases, is quite subject to variation, and accounts for the variation in the results. There seems to be no question as to there being some sort of an influence due to the wall. If we consider Curves 5, 6, and 7, which were obtained by using respectively tubes of wax, rosin and sulphur, with ordinary distilled water, we might say that they represent one general type of wall which gives a relatively small result. Curves 3 and 4 represent the use of Jena glass tubes with ordinary distilled water which give a still larger result. Curve 2 represents the use of Pyrex glass with the same ordinary distilled

water, and gives a still larger result. By grouping the curves in this manner we see that there is a decided influence exerted by the wall. Curves 1 and 8 were obtained, using the same wall but different liquids. The data for Curve 1 was taken, using "extra" distilled water. This water was distilled slowly from a quartz flask heated by means of an electric furnace. Curve 8 represents data taken, using 95% alcohol. These two curves show that the physical properties of the liquid have a marked influence on the values obtained. Curve 1 represents a set of data which gave the maximum value obtained for the ratio of e.m.f. to pressure, and was obtained only once. It appears that in this case we obtained a very pure sample of water which could not be produced the second time.

A few experiments were performed using the electrosmotic effect. Using at first a Pyrex tube built into a crude piece of apparatus, and e.m.f.s up to 500 volts furnished by a dynamo electric generator slightly more than noticeable effects were produced. When a static machine was used in the place of the generator a difference of pressure of about 2 millimeters of water was produced. Later, a piece of apparatus similar to that used by Perrin, shown in Fig. 4, Plate II, was constructed. In the place of the diaphragm C of Perrin was sealed the Pyrex tube. The end of the tube B was led off into a horizontal capillary tube as used by Perrin, and by the displacement of the water in this capillary tube and the corresponding change in level of the liquid in A, a pressure was produced. Although quite large displacements of the meniscus in the capillary tube were obtained by this method, in some cases up to 15 cm., the measurement of the current and electromotive force was impossible. Further, the displacements of the meniscus were

never duplicated due to the effect of surface tension in the capillary tube.

To eliminate these difficulties the apparatus shown in Figure 2, Plate III, was constructed, in which a capillary tube A is sealed between the tubes B and C. The tube A is 1 millimeter in diameter, and 41 centimeters long. The tubes B and C are about 11 millimeters in diameter, so chosen to eliminate, as far as possible, the effect of surface tension. Platinum electrodes were placed in the tubes B and C and the apparatus filled with a liquid to be studied, and allowed to come to hydrostatic equilibrium. An e.m.f. between 500 volts and 2100 volts furnished by the small dynamo electric generators of the corona laboratory, was applied, and a change in level in the tube B when the current was reversed was measured by means of a cathetometer. This gave a difference in level twice as great as that due to the e.m.f. applied in only one direction. The e.m.f. was measured by means of an electrostatic voltmeter, and the current by means of a galvanometer. A modification of this apparatus was constructed, in which 250 c.c. beakers were put in place of tubes B and C. This apparatus was to be used in studying the volume transfer of the liquid, but no results of value were obtained.

By the use of the apparatus first described the results given in Table XII were obtained. It will be seen that the pressures are quite small and that in some cases they are quite irregular. It is to be noted, however, that the pressure decreases as the concentration increases, and that the transfer is always in the direction from the positive to the negative. The maximum pressure was reached quite slowly. The rate of change of pressure decreased rapidly upon application of the e.m.f.. The maximum pressure was

reached in from 1 minute to 2 minutes. It is to be noted that KOH gives in general larger results than HCl, and in the case of dilute solutions gives even larger results than pure water. These results have only a qualitative value as it was not possible to repeat them with exactness. The one outstanding result of this series of experiments is that the transfer is always in the direction of the positive current. This direction is in conformity with the theory of Helmholtz if we assume the liquid to be positively charged with regard to the wall of the tube.

These experiments do not prove Perrin's theory to be without basis, but they make a modification of his theory necessary. We may consider that the behavior of KOH in the experiments on electrosmosis give some support to the explanation of Perrin. We might combine in a way the views of Perrin and Helmholtz by saying that the theory of Helmholtz applies directly to the problem when no ions are present, and with a modification such as suggested by Perrin when there are ions present. It is also true that there is not an exact duplication of the work of Perrin in these experiments but there is at least enough similarity to show that there is a disagreement in some way between the two points of view.

The exact nature of the potential of contact as involved in the phenomena associated with electrosmosis is still a matter for discussion. If we accept the Helmholtz theory we must determine the specific resistance, dielectric constant, and viscosity of the liquid in the region of the double-layer in order to determine the exact value of the potential of contact. In order to prove or disprove the modification offered by Lamb we must know the value of either $\phi_i - \phi_a$ or l/d . This will involve a different relation

involving either of the two quantities. The determination of l/d involves more exact work than has been done and will call for more constant conditions than we have so far been able to obtain. On the whole the solution appears to be difficult, but if found will be a decided advance in the understanding of contact electrical phenomena.

TABLE XI

Data taken at the University of Illinois, 1919-1920.

| Tube | Liquid | Length
in mm. | Diameter
in mm. | e.m.f.
Volts | Pressure
cm. of Hg. |
|----------------|--------------------------------|------------------|--------------------|-----------------|------------------------|
| Data 1 | | | | | |
| Pyrex
Glass | Water
"extra"
distilled | 700 | .95 | 2.9 | 3.65 |
| | | | | 2.59 | 3.25 |
| | | | | 2.39 | 3.05 |
| | | | | 2.21 | 2.82 |
| | | | | 2.02 | 2.48 |
| | | | | 1.84 | 2.32 |
| | | | | 1.66 | 2.12 |
| | | | | 1.49 | 1.89 |
| | | | | 1.32 | 1.65 |
| | | | | 1.15 | 1.40 |
| | | | | 0.98 | 1.19 |
| | | | | 0.82 | 1.06 |
| | | | | 0.65 | 0.84 |
| | | | | 0.44 | 0.52 |
| | | | | 0.32 | 0.30 |
| | | | | 0.238 | 0.20 |
| Data 2 | | | | | |
| Pyrex
Glass | Ordinary
distilled
water | 300 | .90 | 1.27 | 11.4 |
| | | | | .80 | 7.2 |
| | | | | .46 | 3.8 |
| | | | | .31 | 2.4 |
| | | | | .22 | 1.8 |
| Data 3 | | | | | |
| Jena
Glass | Ordinary
distilled
water | 246 | .92 | .985 | 27.4 |
| | | | | .995 | 31.5 |
| | | | | .380 | 10.8 |
| | | | | .61 | 18.9 |

TABLE XI continued

| | Tube | Liquid | Length
in mm. | Diameter
in mm. | e.m.f.
Volts | Pressure
cm. of Hg. |
|--------|---------------------------|--------------------------------|------------------|--------------------|----------------------------------|--------------------------------------|
| Data 4 | Jena
Jena
Glass | Ordinary
distilled
water | 100 | .92 | .76
.35
.14
.03
.85 | 21.7
8.0
3.0
1.0
26.1 |
| Data 5 | Bank of
England
wax | Ordinary
distilled
water | 150 | .5 | .25
.35
.51
.61
.70 | 13.8
18.7
26.8
31.7
36.7 |
| Data 6 | Rosin | Ordinary
distilled
water | 160 | .5 | .355
.148
.610
.675 | 20.6
9.4
37.5
40.3 |
| Data 7 | Sulphur | Ordinary
distilled
water | 160 | .5 | .400
.52
.47
.32
.20 | 26.7
37.3
32.2
19.1
9.8 |
| Data 8 | Pyrex
Glass | Alcohol
95% | 700 | .9 | .13
.16
.17
.12
.10 | 28.0
33.0
30.7
21.4
15.5 |

Note: "Extra" distilled water is water distilled from quartz flask.
 Ordinary distilled water is water distilled from tin-lined
 still.
 Data is given in order taken.

TABLE XII

| E.M.F.
Volts | Current
Amperes
$\times 10^6$ | Pressure
mm. of
water | Solution | Concentration |
|-----------------|-------------------------------------|-----------------------------|------------|---------------|
| 2100 | 1.62 | .40 | Pure water | |
| 2100 | 28.4 | .33 | HCl | N/3300 |
| 2100 | 318.0 | .10 | HCl | N/330 |
| 2100 | 90.6 | .22 | HCl | N/1100 |
| 2100 | 5.36 | .38 | KOH | N/4350 |
| 2100 | 5.42 | .48 | KOH | N/4350 |
| 2100 | 26.5 | .33 | KOH | N/1450 |
| 2100 | 91.5 | .40 | KOH | N/435 |

Note: The transfer was always from the positive to the negative electrode.

Under pressure is indicated the total movement of the meniscus in tube B, Figure 2, Plate III, when the current is reversed.

PART IV

Summary

These investigations have shown the following:

1. With "extra" distilled water and glass of low solubility an e.m.f. of .79 volts per centimeter of mercury pressure is possible. With ordinary distilled water the e.m.f. per unit pressure was found to be lower. We infer that the purer the water the higher the e.m.f. per unit pressure, other things being constant.

2. Experiments performed with tubes of different kinds of glass, rosin, sealing wax, and sulphur, show that the e.m.f. depends upon the nature of the wall.

3. The temperature effect is zero.

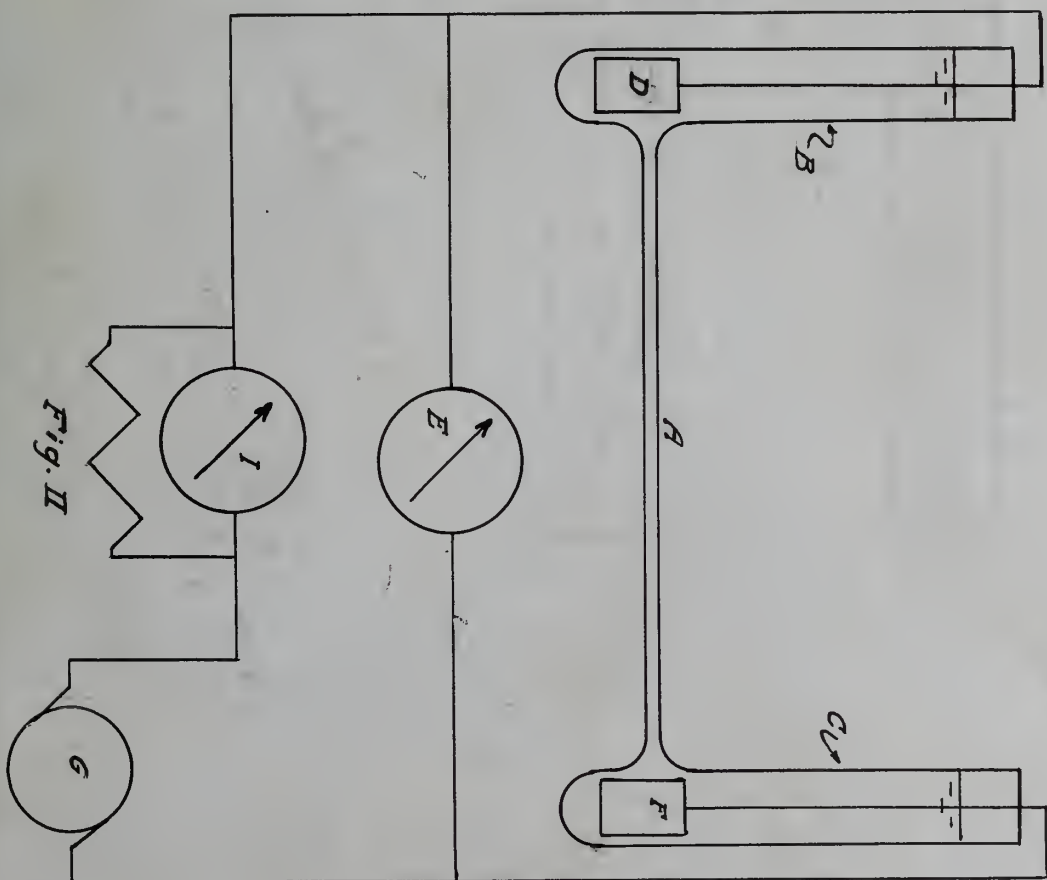
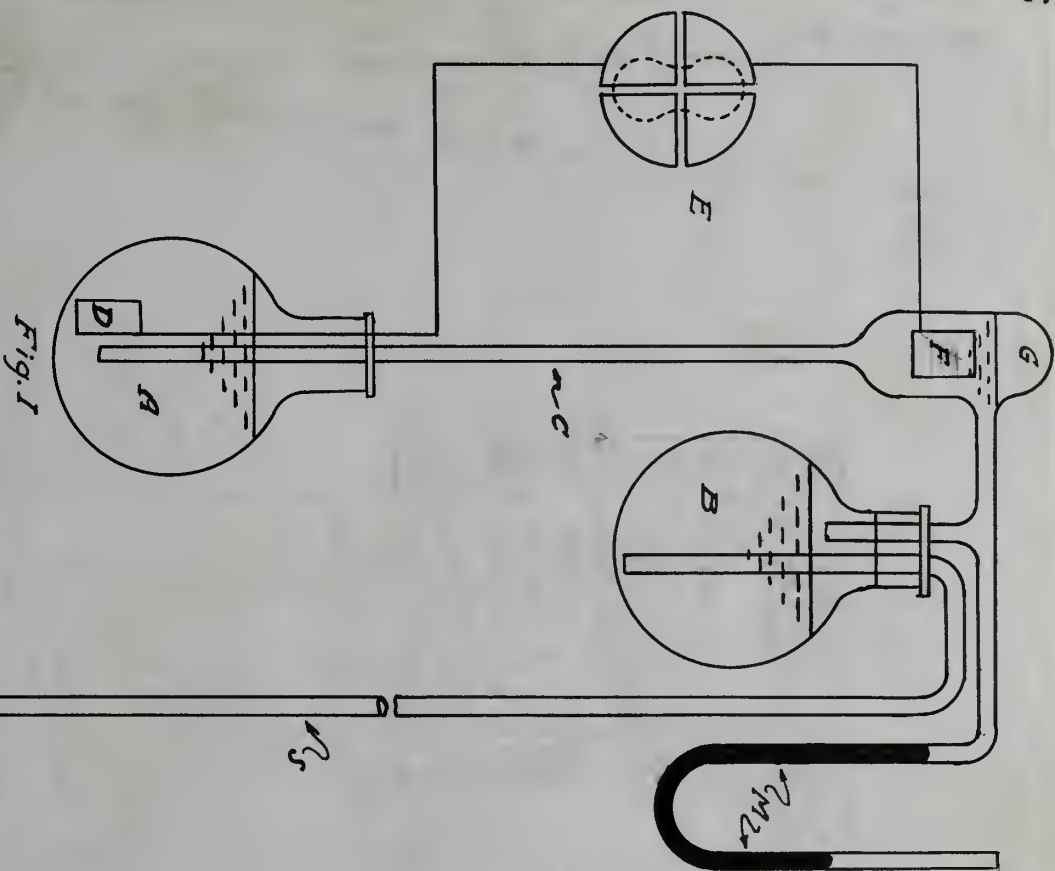
4. By the use of a few different liquids it was found that the physical properties of the liquid must have some bearing upon the results.

5. An attempt to repeat the experiments of Perrin with dilute

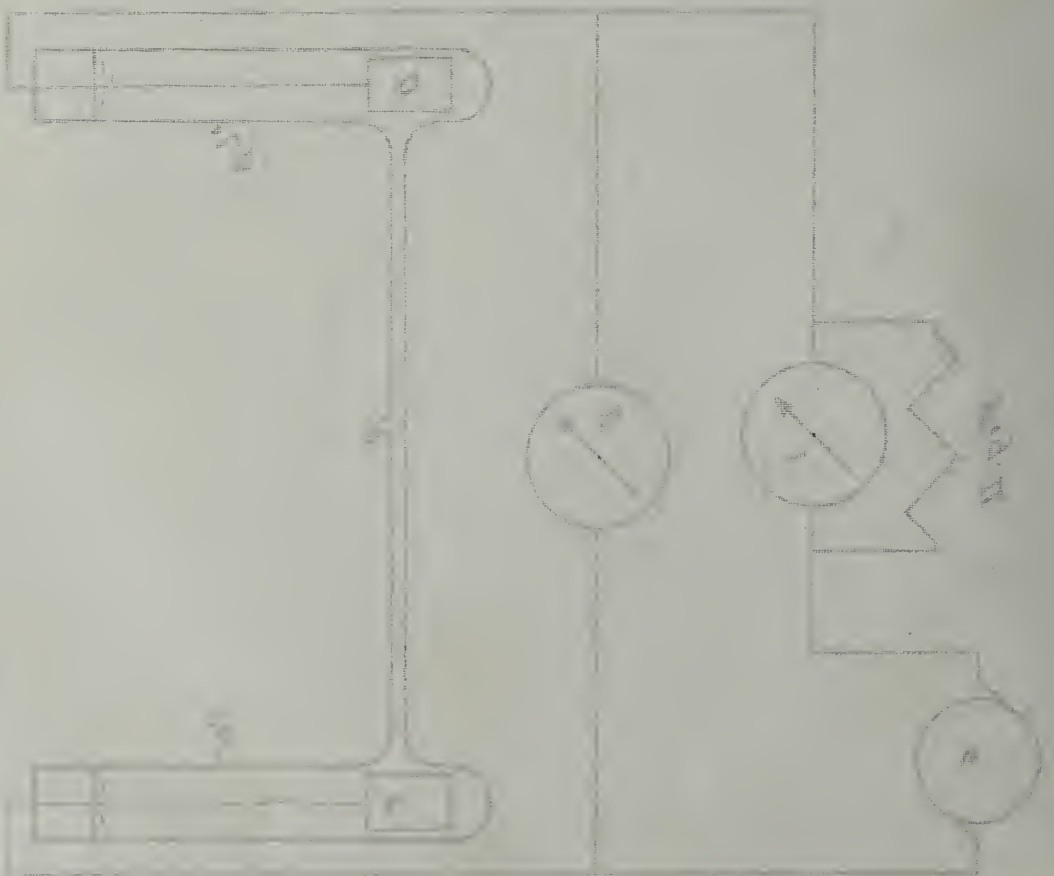
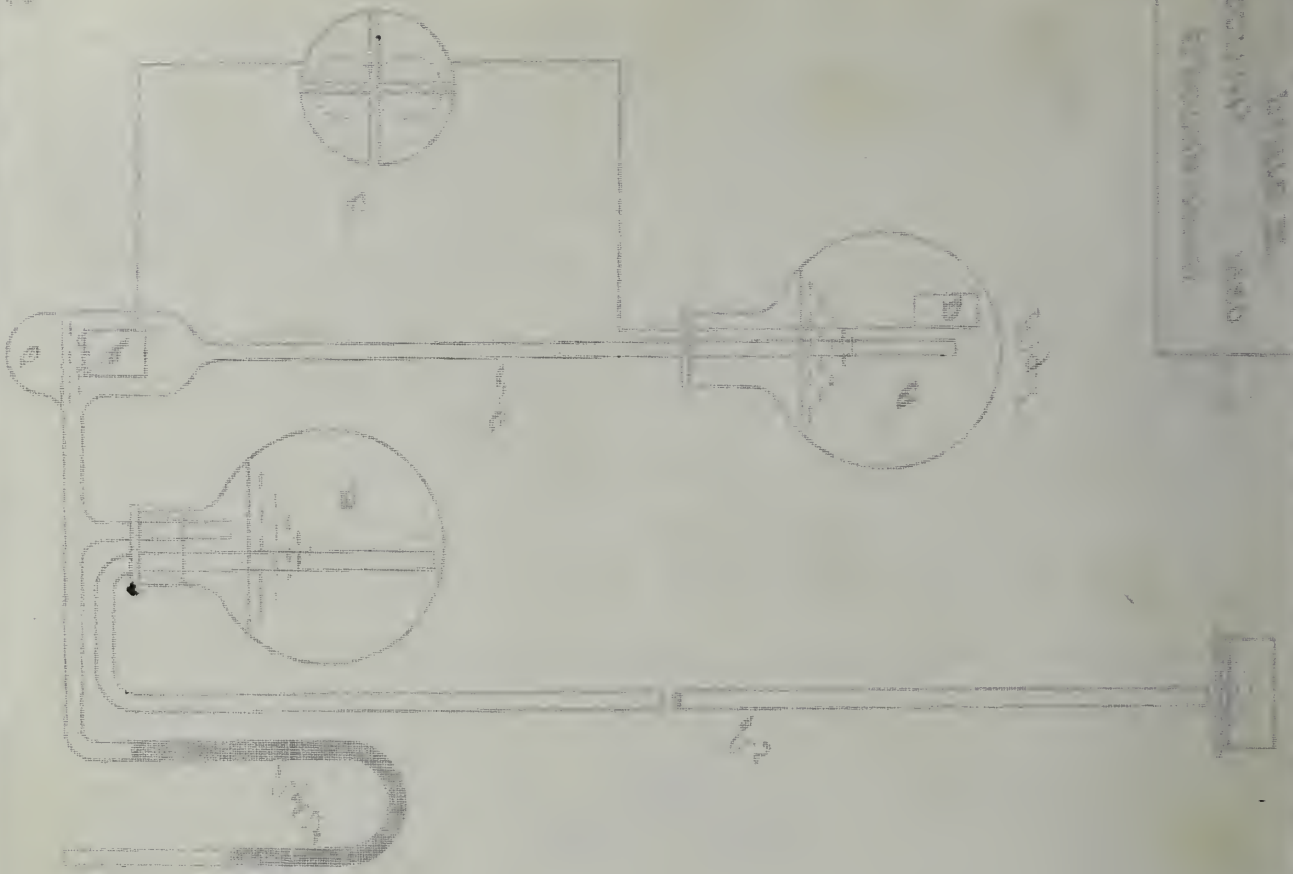
solutions has led to uncertain results. The quantities to be observed are very small and seem to be irregular in value. The experiments show, however, that the effect does vary with the concentration of the solution and the nature of the solute. This should be investigated not only with various liquids, but also by varying the walls with each liquid so as to discover the laws governing the effect with a variation of both liquid and wall.

6. The results under No.1 and No.2 are against Perrin's general conclusion that the effect is due to the liquid and independent of the material of the wall. They agree with the theory of Helmholtz.

The author wishes to express his appreciation of the valuable assistance kindly given by Professor A.P. Carman in his direction of this investigation, and for the use of the facilities of the laboratory.

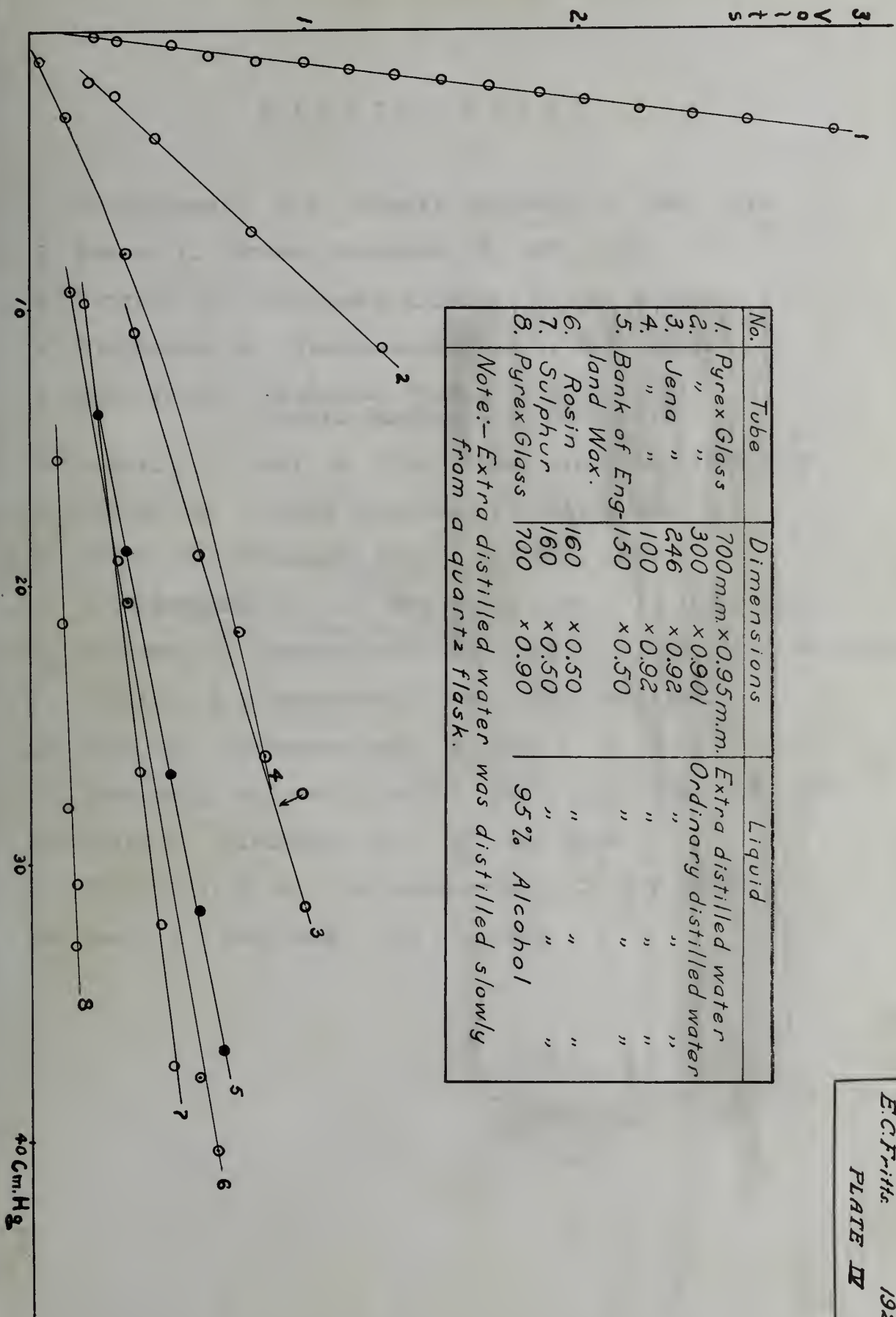


1000
 1000
 1000



| No. | Tube | Dimensions | Liquid |
|-----|---------------------------|--------------------|--------------------------|
| 1. | Pyrex Glass | 700m.m. x 0.95m.m. | Extra distilled water |
| 2. | " " | 300 " x 0.901 | Ordinary distilled water |
| 3. | Jena " | 246 " x 0.92 | " " |
| 4. | " " | 100 " x 0.92 | " " |
| 5. | Bank of Eng-
land Wax. | 150 " x 0.50 | " " |
| 6. | Rosin | 160 " x 0.50 | " " |
| 7. | Sulphur | 160 " x 0.50 | " " |
| 8. | Pyrex Glass | 700 " x 0.90 | 95% Alcohol |

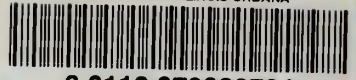
Note:—Extra distilled water was distilled slowly from a quartz flask.



B I B L I O G R A P H Y

- 1 Smoluchowski, M.V. Graetz Handbuch. 2, 366, 1912.
- 2 Reuss, F. Graetz Handbuch, 2, 366, 1912.
- 3 Porrett, R. Thomson's Annalen, 8, 74, 1816.
- 4 Wiedemann, G. Wiedemann Elek., 1, 923, 1893.
- 5 Quincke, G. Wiedemann Elek., 1, 1003, 1893.
Graetz Handbuch, 2, 369, 1912.
- 6 Perrin, J. Jour. d. Chim. Phys., Vol.2&3, 1904,1905.
- 7 Freund, C. Graetz Handbuch, 2, 368, 1912.
- 8 Kühne, R. Wiedemann Elek., 1, 1002, 1893.
- 9 Bois-Reymond, E. du. Wiedemann Elek., 1, 1002, 1893.
- 10 Quincke, G. Poggendorff Ann., 107, 1, 1859; 110, 38, 1860.
- 11 Zöllner, F. Poggendorff Ann., 148, 640, 1873.
- 12 Dorn, E. Wiedemann Ann., 9, 513.
- 13 Cameron, A. and Oettinger, E. Phil. Mag., 234, 586, 1909.
- 14 Saxen, U. Wiedemann Ann., 47, 46, 1892.
- 15 Helmholtz, H. v. Wiedemann Ann., 7, 337, 1879.
- 16 Lamb, H. Phil. Mag., 25, 57, 1888.

UNIVERSITY OF ILLINOIS-URBANA



3 0112 079828734